Supporting Information

Fully exploited imidazolium bromide for simultaneous resolution of cathode and anode challenges in zinc-bromine batteries

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Section A. Materials

All reagents and solvents were of analytical grade and purchased from commercial suppliers including 1-methyl-3-propylimidazolium bromide (MPIBr, 99%; Meryer), $ZnSO_4 \cdot 7H_2O$ (99.5%; Aladdin), $ZnBr_2$ (98%; Aladdin), acrylamide (AR; Chengdu Kelong Chemical Reagent Co. Ltd), ammonium persulfate (98%; Adamas-beta), N,N'-Methylenebisacrylamide (99%; Adamas-beta), N, N, N', N'-tetramethylethylenediamine (99%; Adamas-beta), Zn foil (50 µm or 100 µm; Suzhou Wingrise Energy Technology Co. Ltd.), CNT paper (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences), and used without further purification.

Section B. Experimental section

Preparation of electrolytes. The $ZnSO_4$ electrolyte was prepared by dissolved $ZnSO_4 \cdot 7H_2O$ in DI water with a concentration of 1 mol/kg (1 m). $ZnSO_4$ -MPIBr electrolyte was prepared by adding different concentrations of MPIBr in 1 m $ZnSO_4$ solution while stirring for 30 min.

Preparation of Zn-Br₂ batteries. The Zn-Br₂ batteries were assembled in homemade cells. Carbon nanotube (CNT) paper, with a thickness of 10 μ m, served as the current collectors, and the distance between the two current collectors is approximately 1 cm. The cell contained about 1 mL of ZnSO₄–MPIBr electrolyte. During the charging process, Zn and Br₂ were generated and deposited on the current collectors to form the anode and cathode, respectively. For the pouch cell, the CNT papers as current collectors were cut into 3 cm × 3 cm, and the glass fiber separator was cut into 3.5 cm × 3.5 cm.

Preparation of in-plane interdigitated Zn-Br₂ **micro-batteries.** 6 g of acrylamide was dissolved in 20 mL of DI water with stirring to form a homogeneous solution. Then, ammonium persulfate (20 mg), N,N'-Methylenebisacrylamide (3 mg), and N, N, N', N'- tetramethylethylenediamine (15 μ L) were added to the solution under stirring. The mixed solution was quickly poured into a PTFE mold, sealed, and heated at 50 °C for 12 hours to obtain the polyacrylamide (PAM) hydrogel. The PAM hydrogel was further dried at 80 °C for 12 hours to obtain the dry PAM gel. Subsequently, the dry PAM gel was immersed in ZnSO₄–MPIBr electrolyte for 3 days to obtain the electrolyte hydrogel. A flexible CNT paper was adhered to polyimide tape. Subsequently, interdigitated microelectrodes were created using the laser engraving method. Each microelectrode has a width of approximately 500 μ m, a length of 0.3 cm, and a spacing of 300 μ m between adjacent fingers. Finally, hydrogel electrolyte was applied onto the microelectrode to obtain the in-plane interdigitated Zn-Br₂ micro-batteries.

Section C. Methods

Material characterizations. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku MiniFlex 600 diffractometer with Cu Ka radiation (l = 0.154056 nm) in the range

of 5°-90° or 30°-50°. Field-emission scanning electron microscopy (FESEM) images were obtained on a Thermo Fisher Scientific (FEI) Apreo S HiVoc electron microscope. Aberrationcorrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM) images were collected on a FEI-Titan Themis G2 operated at 300 kV, equipped with double aberration correctors. FTIR spectra were recorded on a Bruker ALPHA spectrometer with a transmission range of range 400-4000 cm⁻¹. The Raman spectra were recorded on a Thermo Fisher Scientific DXR Raman Microscope (455 nm radiation). X-ray photoelectron spectroscopy (XPS) measurements on cycled electrodes were conducted with an AXIS Supra+ (Kratos with a focused 20-500 µm diameter beam of monochromatic X-rays and a 15 kV filament voltage source energy). The Al Ka radiation with an energy of 1486.3 eV and an angle of 0° of emission was used for the measurements. AFM-IR measurements were performed on a Nano-IR2 system from AnaSys. The Zn K-edge X-ray absorption fine structure (XAFS) spectra were carried out using the RapidXAFS 1M (Anhui Absorption Spectroscopy Analysis Instrument Co., Ltd.) by transmission mode at 20 kV and 40 mA. Time-of-Flight secondary ion mass spectrometry (ToF-SIMS) analysis was performed using a PHI nanoTOFI Time-of-Flight SIMS equipped with a 30 kV Bi-cluster liquid metal ion gun (LMIG). Depth profile experiments are carried out using a 3 kV Ar⁺ gas gun for etching with a sputtering rate of about 20 nm/min on SiO₂, a DC current of 100 nA and a sputtered area of 400 μ m \times 400 μ m.

Electrochemical measurements. Electrochemical tests of Zn||Zn and Zn||Cu cells were assembled in 2032-type coin cells. Zn and Cu foil, each with a diameter of 12 mm, were employed as the electrodes, and a glass fiber separator (GE-Whatman) was used. The cells were assembled in an open environment with 120 μ L electrolyte. The discharge–charge curves were recorded on a Neware battery test system (Neware, Shenzhen, China). Cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) were conducted on the Metrohm VIONIC electrochemical workstation. The hydrogen evolution reaction (HER) performance was evaluated using a linear potential scan in Zn||Ti cells with Na₂SO₄ and Na₂SO₄–MPIBr electrolyte at a scan rate of 1 mV s⁻¹. The anti-corrosion test of the Zn foil in different electrolytes was evaluated by performing linear potential scan with a potential range of -0.5 V and 0.5 V (vs. Zn/Zn²⁺) at a scan rate of 5 mV s⁻¹. The pouch cell was initially galvanostatically charged to 20 mA h and subsequently discharged to 0.5 V.

Computational Methods.

Gaussian: Gaussian 16 software¹ is used for the free energy calculation of solvated structures and the binding energy calculation within the framework of DFT. All the molecular structures were computed with the B3LYP (Becke, three-parameter, Lee–Yang–Parr) hybrid functional²

to describe the exchange–correlation energies. The effective core pseudopotentials were used to treat the core electrons. Two basis sets were employed for high-level B3LYP calculations, with the Los Alamos LANL2DZ^{3, 4} applied for the Zn atom while the basis set at 6- $311G^{++}(d,p)^5$ was adopted for other atoms, including C, O, Br, and H.

Density functional theory: Density functional theory (DFT) calculations are performed using the Vienna Ab initio Software Package (VASP) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and projected enhancement wave (PAW) method.⁶⁻⁸ The input structures for the DFT calculations are provided in the Supporting Information as "DFT files". The cutoff energy of the plane-wave basis set is set to 520 eV. The electrode surface in realistic water solvent environments was investigated using the VASPsol package, employing an implicit solvation model.^{9, 10} The implicit solvation model is used to consider the interactions between aqueous solution ($\varepsilon = 78.4 \text{ F m}^{-1}$) and Zn²⁺ solvation structure.^{11, 12} Super soft pseudopotentials are used to describe the interaction between valence electrons and ion nuclei. Monkhorst–Pack special k-point meshes of 5 × 5 × 1 were proposed to carry out geometry optimization and electronic structure calculation. In the process of geometric optimization, all atoms can relax without any restriction until the convergence thresholds of the maximum force and energy are less than 0.01 eV/Å and 1.0×10^{-5} eV/atom, respectively. A 15 Å vacuum layer was introduced to avoid interaction between periodic images. The adsorbed energy between Zn (002) slab and different molecules (H₂O or MPI⁺) is defined as the following equation:

 $E_{adsorb} = E_{Zn(002)+molecule} - E_{Zn(002)} - E_{molecule}$

where $E_{Zn(002)+molecules}$ is the total energy of Zn (002) slab and molecule, $E_{Zn(002)}$ is the energy of Zn (002) slab, and $E_{molecule}$ is the energy of molecule. To maintain a neutral system and ensure the authenticity of the results, a Br⁻ ion was introduced into the system to calculate the adsorbed energy between the Zn (002) slab and MPI⁺.

Ab initio molecular dynamics (AIMD) simulations: The initial structure for the Ab initio molecular dynamics (AIMD) simulations was generated from classical MD simulations by using the amorphous cell module,¹³ with atom charges assigned based on the Force field. The numbers of water molecules and ions are taken from previous publication¹⁴ and are listed in Table S5. The size of the simulation box for ZnSO₄ and ZnSO₄–MPIBr electrolyte is 41.11 × 41.11 Å³ and 45.47 × 45.47 × 45.47 Å³, respectively. Geometry optimizations were carried out to relax the initially prepared system using the COMPASS II force field^{15, 16} with ultrafine quality parameters (convergence tolerance of energy: 2.0×10^{-5} kcal mol⁻¹, force tolerance: 1×10^{-3} kcal mol⁻¹ Å⁻¹). AIMD simulations for the electrolyte structures were

conducted by VASP within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and projected enhancement wave (PAW) method⁶⁻⁸. The Brillouin-zone integration was sampled by a Γ -centered 1 × 1 × 1 Monkhorst–Pack k-point. All atomic positions were fully relaxed until energy and force reached a tolerance of 1 × 10⁻⁵ eV and 0.03 eV/Å, respectively. The dispersion corrected DFT-D method was employed to consider the long-range interactions.¹⁷ At the beginning of the simulation, the AIMD simulations were performed in an isothermal–isobaric ensemble (NPT)^{18, 19} at 300 K for 10 ps with a 1 fs timestep to ensure system equilibrium. The AIMD simulation was further performed in a canonical ensemble (NVT)^{20, 21} for 50 ps, and the Nose-Hoover thermostat was utilized to maintain a temperature of 300 K, with a time step of 1 fs. Diffusion coefficients and the corresponding coordination structures of Zn²⁺ ions were analyzed through last 25 ps simulation. The radial distribution functions (RDF) and diffusion of all species were analyzed using the Visual Molecular Dynamics (VMD) software package.

Section D. Supplementary Figures



Fig. S1. The solubility of 1 m ZnSO₄ with different concentrations of MPIBr.



Fig. S2. pH of the electrolytes with varying concentration of MPIBr.



Fig. S3. (a) Polarization curves and (b) CE for Zn||Cu cells with different electrolytes at 1 mA cm⁻² with an area capacity of 1 mA h cm⁻². (c) The voltage profiles of symmetric Zn||Zn cells with different electrolytes at 5 mA cm⁻².



Fig. S4. Voltage profiles obtained in Zn||Cu cells with (a) $ZnSO_4$ -MPIBr and (b) $ZnSO_4$ electrolytes.

The cell with ZnSO₄–MPIBr electrolyte exhibits stable polarization in the whole cycles. In contrast, the cell with ZnSO₄ electrolyte shows an obvious increase in polarization voltage after 50 cycles and ultimately fails within 100 cycles.



Fig. S5. XRD patterns of cycled Zn anode in ZnSO₄ and ZnSO₄–MPIBr electrolytes.

Distinct diffraction peaks of $Zn_4(OH)_6SO_4 \cdot 5H_2O$ appeared after cycled in $ZnSO_4$ electrolyte. By contrast, only weak $Zn_4(OH)_6SO_4 \cdot 5H_2O$ reflections were detected in $ZnSO_4$ -MPIBr electrolyte, suggesting the MPIBr can suppress the side reactions.



Fig. S6. (a) Hydrogen evolution reaction (HER) in Na_2SO_4 and Na_2SO_4 -MPIBr measured using linear potential scan at a scan rate of 1 mV s⁻¹ in Zn||Ti cells. (b) Tafel curves of Zn||Zn symmetric cells in ZnSO₄ and ZnSO₄-MPIBr electrolytes.

The Zn||Ti cells in Na₂SO₄–MPIBr exhibit a more negative onset potential and a smaller current density, indicating that MPIBr inhibits hydrogen evolution reactions. Besides, the corrosion potential of the Zn anode in the ZnSO₄–MPIBr electrolyte (0.033 V *vs.* Zn/Zn²⁺) significantly exceeds that of the Zn anode in the ZnSO₄ electrolyte (0.015 V *vs.* Zn/Zn²⁺), demonstrating the heightened corrosion resistance in electrolytes containing MPIBr.



Fig. S7. The voltage profiles of symmetric Zn||Zn cells at the current density of 1 mA cm⁻².



Fig. S8. SEM images of pristine Zn foil.



Fig. S9. SEM images of Zn electrodes after different cycles in $ZnSO_4$ and $ZnSO_4$ –MPIBr electrolytes at 1 mA cm⁻² with 1 mA h cm⁻². Scale bar: 500 μ m.



Fig. S10. 2D confocal images of pristine Zn foil.



Fig. S11. 2D confocal images of cycled Zn foils in (a) ZnSO₄ and (b) ZnSO₄–MPIBr electrolytes after 100 cycles.



Fig. S12. Contact angles on the surface of cycled Zn anodes in (a) $ZnSO_4$ and (b) $ZnSO_4$ -MPIBr electrolytes for 100 cycles.



Fig. S13. In situ optical observation of Zn deposition on Zn foil in $ZnSO_4$ and $ZnSO_4$ –MPIBr electrolytes at a current density of 5 mA cm⁻².

In the $ZnSO_4$ electrolyte, uneven Zn particles aggregate after plating for 5 minutes, with significant Zn dendrites appearing after 15 minutes. Conversely, in the $ZnSO_4$ –MPIBr electrolyte, a relatively smooth surface is achieved throughout the plating process.



Fig. S14. XRD patterns of Zn anodes after deposition for various times at the current density of 10 mA cm^{-2} in (a) ZnSO₄–MPIBr and (b) ZnSO₄ electrolytes.

As the Zn deposition time prolongs, the intensity of the (002) facet in the ZnSO₄–MPIBr electrolyte gradually increases, with the ratio of $I_{(002)}/I_{(101)}$ rising from 0.44 to 0.77, indicating that Zn growth predominantly occurs along the (002) facet. In comparison, the Zn deposition in the ZnSO₄ electrolyte tends to along the (101) facet that is prone to dendritic formation.



Fig. S15. Long-term cycling stability of Zn||Zn symmetric cells at (a) 5 mA cm⁻² with a capacity of 5 mA h cm⁻² and (b) 10 mA cm⁻² with a capacity of 5 mA h cm⁻². Comparison of electrochemical performance of Zn||Zn symmetric cells using recently reported electrolytes with current density of 5 or 10 mA cm⁻².



Fig. S16. Shelving-recovery performance of symmetric Zn||Zn cells.

To replicate real-world conditions for the application of the $ZnSO_4$ –MPIBr electrolyte, the cells were tested for 25 cycles at 1 mA cm⁻² with an area capacity of 1 mA h cm⁻². Subsequently, the cells were shelved for 50 h. The cells with $ZnSO_4$ electrolyte exhibit a sharp polarization increase after a shelving-recovery period of 5 cycles, while the cells with $ZnSO_4$ –MPIBr electrolyte maintain stability throughout the cycling process.



Fig. S17. CV curves of Na_2SO_4 and Na_2SO_4 -MPIBr electrolytes measured using a three-electrode system with Ti foil as the working electrode, Pt plate as the counter electrode, and Ag/AgCl as the reference electrode.



Fig. S18. Schematic illustration of Zn deposition in different electrolytes.



Fig. S19. Raman spectra of 1 m ZnSO₄, 1 m ZnSO₄-0.5 m MPIBr, 1 m ZnSO₄-1 m MPIBr, and 1 m ZnSO₄-2 m MPIBr.



Fig. S20. FTIR spectra of 1 m ZnSO₄, 1 m ZnSO₄–0.5 m MPIBr, 1 m ZnSO₄–1 m MPIBr, and 1 m ZnSO₄–2 m MPIBr.



Fig. S21. The binding energies of Zn^{2+} with H_2O and Br^- .



Fig. S22. Energy and temperature evolution versus the AIMD time of different electrolyte systems during NPT for 10 ps at 300 K. (a) ZnSO₄ and (b) ZnSO₄–MPIBr electrolyte.



Fig. S23. (a) 3D snapshots of $ZnSO_4$ electrolyte obtained from AIMD simulations. (b) Radial distribution function and coordination numbers of Zn^{2+} -O (H₂O) and Zn^{2+} -O (SO₄²⁻) in ZnSO₄ electrolyte.



Fig. S24. The distribution of the solvation structures in (a) ZnSO₄ and (b) ZnSO₄–MPIBr electrolytes.



Fig. S25. Current-time plots of Zn symmetric cells with (a) ZnSO₄ and (b) ZnSO₄–MPIBr electrolytes at a constant potential of 0.025 V. (inset: EIS tests before and after the polarization)



Fig. S26. The function of MSD vs. time in $ZnSO_4$ and $ZnSO_4$ –MPIBr electrolytes.



Fig. S27. MSD of H₂O molecules in ZnSO₄ electrolyte and ZnSO₄–MPIBr electrolyte.

The diffusion coefficient of H₂O molecules in the ZnSO₄–MPIBr electrolyte $(3.66 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$ is lower than that in ZnSO₄ electrolyte $(2.51 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$. This could be attributed to the interaction between the H₂O molecules and their environment ions (Br⁻/MPI⁺), potentially leading to a sluggish mass transfer of H₂O.²²⁻²⁵



Fig. S28. (a) Nyquist plots collected at open circuit voltage (OCV) over the frequency range of 100 kHz to 0.1 Hz in different electrolytes. (b) Ionic conductivity comparison of different electrolytes.



Fig. S29. Nyquist plots of Zn||Zn cells over the frequency range of 100 kHz to 0.1 Hz at different temperatures in (a) $ZnSO_4$ and (b) $ZnSO_4$ –MPIBr electrolytes.



Fig. S30. Nucleation overpotential comparisons with reported works.²⁶⁻³¹



Fig. S31. Rate performance of Zn ||Zn cells at current densities of 1, 2, 5, 10, and 20 mA cm⁻².



Fig. S32. (a) Voltage profiles and (b) overpotential comparison of Zn||Cu cells at different current densities with $ZnSO_4$ and $ZnSO_4$ –MPIBr electrolytes.



Fig. S33. Voltage profiles of Zn||Cu cells at different current densities with (a) $ZnSO_4$ and (b) $ZnSO_4$ -MPIBr electrolytes.



Fig. S34. CV curves for Zn||SS cells with $ZnSO_4$ and $ZnSO_4$ –MPIBr electrolytes.



Fig. S35. CV curves of the dual-plating Zn-Br₂ batteries based on ZnSO₄–MPIBr electrolyte.



Fig. S36. (a) Coulombic efficiencies and (b) GCD curves of Zn-Br₂ batteries with different electrolytes at current density of 2 mA cm⁻² with a charge capacity of 1000 μ A h cm⁻².



Fig. S37. GCD curves at different charge capacities of the dual-plating Zn-Br₂ batteries.



Fig. S38. Coulombic efficiencies at different charge capacities.



 $\label{eq:Fig.solution} \textbf{Fig.} \quad \textbf{S39.} \quad \text{Rate} \quad \text{performance} \quad \text{of} \quad \text{dual-plating} \quad \text{Zn-Br}_2 \quad \text{batteries.}$



Fig. S40. GCD curves of Zn-Br₂ batteries in different electrolytes at a charge capacity of 6000 μ A h cm⁻².

After charging to 6000 μ A h cm⁻², the discharging areal capacity of the Zn-Br₂ battery containing 2 m MPIBr still reaches 5700 μ A h cm⁻² with a high CE of 95.0%. In contrast, the CEs of Zn-Br₂ batteries with 0.5 m and 1 m MPIBr are only 58.2% and 78.5%, respectively, due to the insufficient MPI⁺ cations to suppress the shuttle of numerous Br_x⁻ species.



Fig.S41.GCDcurveof $Zn-Br_2$ pouchcell.



Fig. S42. Zn-Br $_2$ batteries could power an LED light under different destruction scenarios.



Fig. S43. Photographs of Zn- Br_2 micro-batteries and a temperature and humidity meter powered by Zn- Br_2 micro-batteries.

Movie S1

Successful	takeoff	of	the	drone	powered	by	Zn-Br ₂	pouch	cells.
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Electrolyte	Current density and capacity (mA cm ⁻² ; mA h cm ⁻²)	Coulombic efficiency (%)	Cycle number	Ref.	
ZnSO ₄ +MPIBr	2~1	99.9	2600	This work	
0.3 M zinc gluconate	0.1~0.1	95	~130	Chem. Eng. J., 2023 , 454, 140364	
1 M ZnSO ₄ + 25 mM NHP	1~0.5	99.4	1000	Angew. Chem.Int. Ed. 2023, 62, e202212695	
ZnSO ₄ +CeCl ₃	$10 \sim 10$ $2 \sim 1$	99.7 99.8	60 300	Adv. Mater. 2022, 34, 2203104	
ZnAc ₂ +NH ₄ I (ISE)	—	99.8	100	J. Am. Chem. Soc. 2022 , 144, 18435–18443	
ZnSO ₄ -H ₂ O-NMP	1~1	99.8	1000	Angew. Chem.Int. Ed. 2022 , 61, e202212839	
$Zn(OTf)_2$ in $H_2O +$	1~1	99.8	200	Chem. Sci., 2021, 12,	
DMC	5~2.5	99.8	600	5843-5852	
PEGTE+Zn (CF ₃ SO ₃) ₂	3~3	99.2	350	Nano Lett. 2022 , 22, 8574–8583	
ZnSO ₄ -C ₃ N ₄ QDs	—	99.61	200	Nat. Commun. 2022 , 13, 5348.	
$\alpha\text{-}CD + ZnSO_4$	1~1	99.9	600	J. Am. Chem. Soc. 2022 , 144, 11129–11137	
Zn(ClO ₄) ₂ -β-CD	_	84.9	530	Angew. Chem. Int. Ed. 2022 , 61, e202210979	
β -CD/ZnSO ₄	1~0.5 (52.5 mV)	99.56	1700	Adv. Funct. Mater. 2022, 32, 2207732	
WIL20	1~0.5	99.27	200	ACS Energy Lett. 2023 , 8, 608–618	
ZnSO ₄ +EGME	2~1	99.5	600	Nano Lett. 2023 , 23, 541–549	
DX/ZnSO ₄	10~10	99.7	1500	ACS Nano 2023 , 17, 3765–3775	
Xylitol/ZnSO ₄	1~1	99.6	100	Angew. Chem. Int. Ed. 2023 , 62, e202218872	
Zn(OTF) ₂ -Zn(NO ₃) ₂	1~0.5	99.8	200	Angew. Chem. Int. Ed. 2021, 60, 13035–13041	
0.5 M-Zn(OTf) ₂ - DMMP	1~	99.5	1000	Angew. Chem. 2023 , 135, e202215600	
DDTC/ZnSO ₄	1~1	99.3	700	Energy Environ. Mater.	

Table S1 Comparison of the cycling performance of $Zn \|Cu$ asymmetric cells in various electrolytes.

				2023 , 7, e12608
APA-Zn(OTf) ₂	1~1	99.3	150	Energy Environ. Sci., 2023 , 16, 1662–1675
pyridine-ZnSO ₄	~1	99.6	1800	Angew. Chem.Int. Ed. 2023 , 62, e202303011
2 m ZnSO ₄ + 0.05 m SG	1~0.5	99.1	1000	Adv. Mater. 2022 , 34, 2206963
IL-AE	1~1	99	250	Adv. Mater. 2023 , 35, 2210789
BA/ZnSO ₄	1~0.5	99.57	750	Angew. Chem. Int. Ed. 2022 , 61, e202212780
70SL	4~2	99.9	200	Nat. Commun. 2023 , 14, 3067

Electrolytes	Current density (mA cm ⁻²)	Capacity (mA h cm ⁻²)	Time (h)	Ref.
ZnSO ₄ –MPIBr	5	5	970	This work
ZnSO ₄ -MPIBr	10	5	660	This work
ZnSO ₄ + Pectin	5	5	900	<i>Energy Environ. Sci.</i> 2024, DOI: 10.1039/D4EE00199K.
WSE	5	5	600	Nat. Commun. 2024, 15, 302.
ZSO/DM-0.09	5	5	550	Angew. Chem. Int. Ed. 2024 , e202403050
TW20	5	5	500	<i>Adv. Mater.</i> 2024 , <i>36</i> , 2312924.
[EMIM]OTF/ZnS O4	5	5	900	<i>Adv. Funct. Mater.</i> 2024 , 2314347.
0.1-ASA	5	5	600	Chem. Sci. 2024, 15, 230-237.
TMB-5	5	5	700	Energy Storage Mater. 2024 , 64, 103059.
pyridine-ZnSO ₄	5	5	650	Angew. Chem. Int. Ed. 2023 , 62, e202303011.
Me56	5	5	1000	J. Am. Chem. Soc. 2023 , 145, 22456–22465.
DX/ZnSO ₄	5	5	1000	ACS Nano 2023 , 4, 3765– 3775.
HMTA/ZnSO ₄	5	5	600	Adv. Energy Mater. 2023, 13, 2300550.
ZnSO ₄ -1% Py	5	5	550	Angew. Chem. Int. Ed. 2023 , 62, e2023023.
Zn(ClO ₄) ₂ -β-CD	5	5	350	Angew. Chem. Int. Ed. 2022 , 61, e202210979.
PZIB gel electrolyte	5	5	500	Adv. Sci. 2022, 9, 2104832.
α -CD + ZnSO ₄	5	5	200	J. Am. Chem. Soc. 2022 , 144, 11129–11137.
SG/ZSO	5	1	800	<i>Adv. Funct. Mater.</i> 2024 , 2402484
Zn(CF ₃ SO ₃) ₂ and ZnI ₂ in EG-H ₂ O	5	2.5	300	Energy Environ. Sci. 2023 , 16, 2358–2367.
ZSO-H ₂ O-BA	5	1	968	Energy Environ. Sci. 2024 , 17, 2888-2896.
$ZnSO_4 + DFA$	10	1	900	Adv. Energy Mater. 2023, 13,

Table S2 Comparison of electrochemical performance of the Zn||Zn cells using recently reported electrolytes with current density of 5 or 10 mA cm⁻².

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ZnSO ₄ +TU	10	1	600	Adv. Funct. Mater. 2022, 32, 2206695.
ZnSO ₄ +NTA	10	2	500	<i>Energy Storage Mater.</i> 2023 , <i>63</i> , 102980.
0.1-ASA	10	2	420	Chem. Sci. 2024, 15, 230-237.
α -CD + ZnSO4	10	1	160	J. Am. Chem. Soc. 2022 , 144, 11129–11137.
ZSO-H ₂ O-BA	10	1	800	Energy Environ. Sci. 2024 , 17, 2888–2896.
$ZnSO_4 + DA$	10	1	700	Adv. Funct. Mater. 2024, 2316371.

Electrolyte	Nucleation overpotential (mV)	Ref.
ZnSO ₄ +MPIBr	9	This work
0.3 M zinc gluconate	43	Chem. Eng. J., 2023, 454, 140364
ZnSO ₄ +EGME	17.4	Nano Lett. 2023, 23, 541–549
Xylitol/ZnSO ₄	13.99	Angew. Chem. Int. Ed. 2023, 62, e202218872
α -CD/ZnSO ₄	40.3	J. Am. Chem. Soc. 2022, 144, 11129–11137
Tiron/ZnSO ₄	89	Adv. Funct. Mater. 2023, 33, 2305041
ZSO/DM-0.09	0	Angew. Chem. Int. Ed. 2024, e202403050
$3-Ag^+/ZnSO_4$	16.8	Chem. Eng. J. 2023, 457, 141305

Table S3 Comparison of nucleation overpotential in various electrolytes.

Cathode	Anode	Electrolyte	Current density (mA cm ⁻²)	Cycle number	Retention (%)	Ref.	
Br ₂	CNTs paper	ZnSO ₄ -MPIBr	2	1000	100	This work	
MnO ₂	C/Cu	3 M Zn(CF ₃ SO ₃) ₂	1	80	68.2	Nano Lett. 2021 , 21, 1446–1453	
$Zn_3V_3O_8$	Cu@Cu ₃ Zn network- modified CCF	3 M Zn(CF ₃ SO ₃) ₂	2 A/g	200	80	J. Energy Chemistry 2023 , 76, 32–40	
Graphite	Cu–Ag	3 m Zn(TFSI) ₂ /EMC	0.5 A/g	1000	82%	Adv. Mater. 2022, 34, 2201957	
$Zn_{0.5}VO_2$	Cu@AFO	3 m Zn(OTF) ₂	1 A/g	2000	60	Adv. Energy Mater. 2023 , 13, 2204388	
ZnMn ₂ O ₄	Cu	50% PC-sat.		275	80	J. Am. Chem. Soc. 2022 , 144, 7160–7170	
ZnMO	AgNWA	2 M ZnSO ₄	0.5 A/g	600	73	Energy Storage Mater. 2022 , 51, 453–464	
Cl_2	NIL	1 M ZnSO ₄ -1 M LiCl-0.4 M TMACl	20	200	95	Nano Lett. 2022 , 22, 3298–3306	
Zn _x CVO	gr-Cu	BLE	1 A/g	100	76.7	Energy Environ. Sci., 2022 , 15, 5217–5228	
MnO ₂	ZnA coating Cu	2 m ZnSO ₄ /0.2 m MnSO ₄	2 A/g	90	74.6	Adv. Energy Mater. 2023 , 13, 2203542	

 Table S4 Comparison of electrochemical performance of the anode-free Zn batteries.

Electrolyte	H ₂ O	Zn^{2+}	SO4 ²⁻	MPI ⁺	Br⁻
ZnSO ₄ -MPIBr	2000	36	36	72	72
ZnSO ₄	2000	36	36		

Table S5 | The numbers of water molecules and ions in amorphous cell module.

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